

CHEMICAL EVIDENCE FOR THE BENT EXCITED
STATE OF DIACETYLENE*

By

G. J. Pontrelli

Radiation Physics Laboratory - Engineering Department
E. I. du Pont de Nemours and Company
Wilmington, Delaware

FACILITY FORM 602

CR-62597
(PAGES) 9
(ACCESSION NUMBER)
N 66 81849
(NASA CR OR TMX OR AD NUMBER)

None
(CODE)
(CATEGORY)
(THRU)

Spectroscopic evidence obtained by Woo and Chu^{1,2} and by Callomon³ indicated that diacetylene has two regions of absorption between 2000 and 3000 Å: "high-pressure bands" ($\lambda > 2500 - 2970$ Å); and "low-pressure bands" (≈ 2000 Å $\lambda < 2500$ Å). The complexity of the "high-pressure bands" and the inability to resolve the rotational structure led to the conclusion that diacetylene was predissociated when it absorbed radiation greater than 2500 Å. Woo and Chu suggested further that the excited state produced by absorption at wavelengths greater than 2500 Å might be bent. I wish to report chemical evidence to support the existence of a bent excited molecule of diacetylene when it absorbs radiation at 2537 Å.

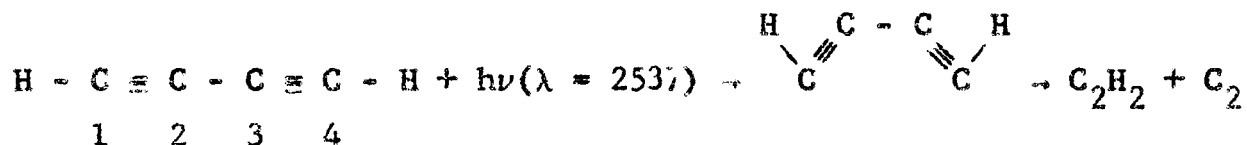
When diacetylene at pressures from 0.1 to 10 mm is subjected to 2537 Å radiation from a Hanovia Type 688845 low-pressure mercury lamp, the only gaseous products observed are acetylene (C_2H_2) and a very small amount of triacetylene (C_6H_2).

* This work was supported in part by the National Aeronautics and Space Administration under Contract No. NAS w-707.

~~Available to NASA only and~~
~~NASA Centers Only.~~

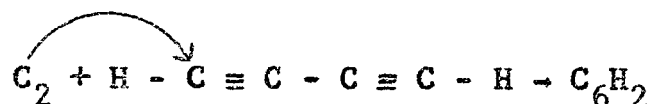
Experiments using completely deuterated propylene mixed in various ratios with diacetylene (1:10 to 10:1) showed by the absence of any C_2HD that the acetylene formation did not occur through the formation of the ethynyl (C_2H) radical. Additional evidence for the absence of a radical mechanism in the formation of acetylene is that addition of nitric oxide does not decrease the acetylene yield. In another paper,⁴ we will show that, at wavelengths below 2500 Å, the formation of acetylene does occur through the formation of the C_2H radical, which then abstracts hydrogen from diacetylene to produce acetylene.

On the basis of the above evidence, we suggest that, at wavelengths above 2500 Å, the acetylene is formed through the molecular elimination of C_2 from the bent excited molecule, leaving acetylene as a gaseous product. The sequence can be visualized as follows:



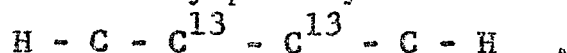
The actual process of bond breaking and formation must be extremely complicated and cannot be specified with the available data.* It would be of interest to determine the molecular orbitals and symmetry of this excited state.

The formation of triacetylene (C_6H_2) gives additional evidence for the formation of C_2 . One can postulate an insertion reaction by C_2 into the C-H bond in a manner similar to the methylene radical,^{5,6} viz.,

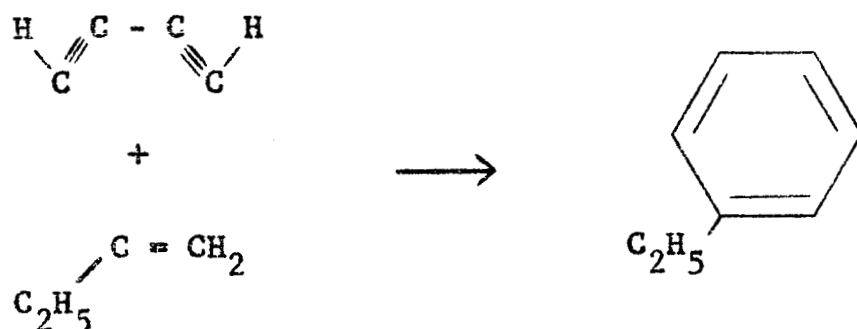
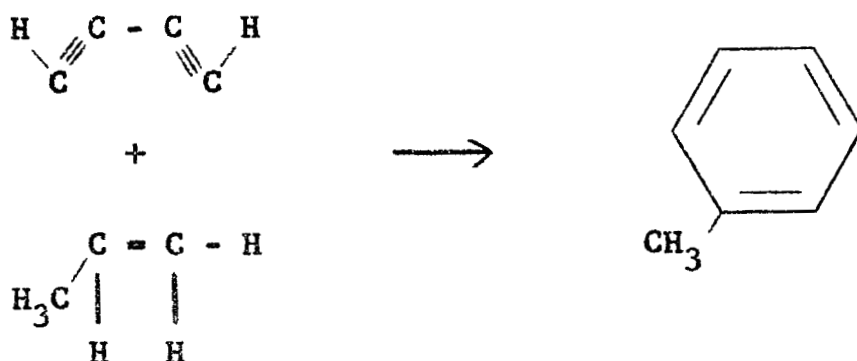


Further evidence for the bent excited state was obtained when mixtures of diacetylene and propylene (at ratios ranging from 1:1 to 1:10, respectively, at total pressures less than 2 mm) were irradiated with 2537 Å mercury radiation and produced toluene. The samples were irradiated for 1 hr, and the gas-phase products were analyzed by a Bendix time-of-flight mass spectrometer. A similar reaction occurred when a 1:1 mixture of diacetylene and butene-1 was irradiated. In this case, the formation of ethylbenzene was

* The possibility of C_2H_2 formation by hydrogen atom migration with subsequent elimination of carbon to form C_2 could be checked by photolysis of isotopic diacetylene, viz.,



observed. The formation of toluene and ethylbenzene involving the bent excited diacetylene molecule can be visualized as follows:



In both cases, a breaking and formation of new bonds with hydrogen atom transfer is required. The reaction between butene-2 and diacetylene yielded xylene. We were not, however, able to determine, mass spectrometrically, whether we formed o, m, or p-xylene and obtain information about the methyl and/or hydrogen migration. Based on the number of

photons absorbed by diacetylene, the quantum yield for formation of these aromatic molecules are all on the order of 10^{-3} for 1:1 mixtures.

Table I lists the mole percent of products formed relative to the moles of diacetylene reacted for a 1:1 mixture of diacetylene and propylene.

TABLE I

| <u>Product Formed</u> | <u>Mole % Formed From Reacted Diacetylene</u> |
|-------------------------|---|
| C_7H_8 (toluene) | 3 |
| C_6H_2 (triacetylene) | 2 |
| C_2H_2 (acetylene) | 20 |
| Polymer Formed | 75 |

REFERENCES

1. S. C. Woo and T. C. Chu, J. Chem. Phys. 3, 541 (1935).
2. S. C. Woo and T. C. Chu, J. Chem. Phys. 5, 786 (1937).
3. J. H. Callomon, Can. J. Phys. 35, 129 (1957).
4. To be published.
5. J. W. Simons and B. S. Rabinovitch, J. Am. Chem. Soc. 85, 1023 (1963).
6. H. M. Frey, Trans. Faraday Soc. 58, 516 (1962).